(19) Europäisches Patentamt
European Patent Office
Office européen des brev ts

(11) Publication number: **0 109 366**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **83830204.0**

(22) Date of filing: **18.10.83**

(51) Int. Cl.³: **C 10 M 11/00**, A 62 D 3/00

(30) Priority: **11.11.82 IT 2417482**

(43) Date of publication of application: **23.05.84 Bulletin 84/21**

(84) Designated Contracting States: **AT BE CH DE FR GB LI LU NL SE**

(71) Applicant: **D.E.L.C.O. di COPPO Ing.Mario, Via Umberto I ,n.1, I-20012 Cuggiono (Milano) (IT)**

(72) Inventor: **Coppo, Mario, Via Solferino, n. 10, Inveruno (MI) (IT)**

(74) Representative: **Calvani, Domenico, UFFICIO BREVETTI ING. CALVANI, SALVI & VERONELLI 4, Piazza Duca d'Aosta, I-20124 Milan (IT)**

(54) **M thod of decontaminating mineral oils and dielectric silicone fluids.**

(57) The method comprises mixing the fluid to be decontaminated with a solvent at a temperature suitable for a full dissolution thereof, separating by decantation and/or centrifugation the solvent excess from the fluid under treatment, stripping the dissolved rests of solvent from the fluid and recovering the solvent by distillation under separation of the polychlorobiphenyl originally contained in the fluid to be decontaminated.

A pyrrolidone or an alkylderivative thereof is employed as a solvent. The mixing, decantation and/or centrifugation and stripping steps can be cyclically repeated until the fluid is fully deconctaminated.

EP 0 109 366 A1

0109366

T I T L E

"METHOD OF DECONTAMINATING MINERAL OILS AND DIELECTRIC SILICONE FLUIDS"

Applicant: D.E.L.CO di Coppo Ing.Mario
Via Umberto 1° N.1 CUGGIONO (Milano)

Inventor : Mario Coppo

The present invention relates to a method of decontaminating mineral oils generally and dielectric silicone fluids from polychlorobiphenyl by means of a solvent.

As known, for antifire purposes, fluids on the basis of polychlorobiphenyl (PCB) have been often used in the past as insulating fluids in electric equipment. These fluids, generally a mixture of 40% of trichlorobenzene and 60% of polychlorobiphenyl, exhibit very good antifire properties which assure a reliable operation of electric equipment even in environments in which the fire conditions could be promoted.

For example, there are in Italy only tens of thousands of transformators, circuit breakers and other electric equipment still filled with this fluid and an undefined number of hydraulic apparatus almost certainly still contamined by PCB.

The suspected cancerous action or at any rate the harmfulness of PCB has caused the use of these fluids in the above mentioned equipment to be suspended, which fluids are gradually substituted by other less dangerous fluids.

The aggressiveness of fluids on the basis of PCB towards the components of the electric equipment is so great that its decontamination becomes an extremely difficult operation and the high harmfulness thereby exhibited causes it to be more convenient to bury all equipment into suitably prepared pits than to try a decontamination thereof.

Of course, for economical reasons, this has given rise to the problem of the recovery of the equipment by trying to decontaminate it as much as possible, by reducing the PCB contents at least within limits which are permissible and tolerable from ecological standpoint. However, since the PCB absorbed by materials, such as paper and wood, which are normally present in the electric equipment and the PCB adsorbed by the inner portion of the magnetic lamination pack or the electric windings cannot be totally removed, at least in a short time, because of its aggressiveness, a portion thereof remains attached to these equipment portions so that, with the passing of tim , it dissolves in the new fluid used in substitution thereof, which in turn, is contaminated by PCB, thereby forming a source of contamination and danger for the operators.

It is therefore an object of the present invention to obviate the above mentioned disadvantages by providing a new method permitting the dielectric fluids used in substitution of polychlorobiphenyl and contaminated thereby because introduced within not fully decontaminated equipment to be decontaminated as much as possible, however within ecological acceptable limits so that the equipment can be reused.

It is another object of the pr sent invention to provide a PCB decontaminating method which can be carried

out without the intervention of operators in contact with PCB.

It is a further object of the present invention to provide a method of the above mentioned kind, which performs a quickly decontaminating action so as to result very unexpensive and which can be carried out as simply as possible without requiring sophisticated and expensive equipment.

These and other objects of the present invention which will appear more evident in the course of the following description are attained by a method of decontaminating mineral oils and dielectric silicone fluids from polychlorobiphenyl which, according to the invention, is characterized in that it comprised the steps of:

- mixing the fluid to be decontaminated with a suitable solvent at a suitable temperature in order to dissolve the polychlorobiphenyl and the possible oxidized compounds;
- separating by decantation and/or centrifugation the solvent excess from the fluid under treatment,
- stripping from the fluid the dissolved rests of solvent and
- recovering the solvent by distillation and separating polychlorobiphenyl therefrom.

According to a feature of the invention, the dissolving step of polychlorobiphenyl and possible oxidized compounds contained in the fluid to be decontaminated occurs at a temperature ranging from 50° to 80°C.

According to another feature of the invention, the

stripping step occurs under vacuum and in an atmosphere of inert gas, preferably nitrogen.

Suitably, the mixing and dissolving, decantation and/or centrifugation and/or stripping steps can be sequentially repeated until the fluid will be fully decontaminated.

Preferably, the solvent is in the liquid condition at the operative temperature in order to facilitate its mixing with the fluid to be decontaminated and further it has a good heat-stability, a good water miscibility, a very small toxicity and a very low cost.

As a further feature, the solvent has a lower boiling temperature both than that of the fluid to be decontaminated and that of PCB in order that it can be readily recovered for reuse, this temperature being however higher than the operative temperature.

Advantageously, the solvent has a higher density than that of the fluid to be decontaminated in order to facilitate the decantation and/or centrifugation steps.

Suitably, the solvent has a low solubility towards the components of the fluid under treatment and a good affinity to the biphenylchlorinated and oxidized compounds.

According to the invention, a pyrrolidone or an alkylderivative thereof is employed as a solvent such as 1-methyl -2-pyrrolidone or 2-pyrrolidone.

The invention will now described in more detail in connection with a preferred embodiment thereof given merely by way of example and therefore not intended in a limiting sense, illustrated in the accompanying drawing, wherein the sole Figure is a schematic showing of a system

for carrying out the m thod according to the invention.

As can be seen from the figure, th oil O under treatment is pumped by a circulating pump PC1 through a three-way valve V1, into a static mixer M, in which the pyrrolidone is fed through a line 3 and the so obtained mixture is caused to flow into a set of heaters R1, which are thermostatically controlled at a temperature of 50° to 80° C so as to dissolve the polychlorobiphenyl and the possible oxidized compounds contained in the fluid under treatment in the pyrrolidone.

Then, the mixture flows out of the set of heaters R1 and through a serv-ovalve V2, enters the centrifuge C, where the pyrrolidone is separated and fed, through a line 4, to the pyrrolidone storage tanks SP1, SP2, through a three-way valve V5. Then the oil separated by the centrifuge C, having still a 2% of pyrrolidone content, is caused to flow through a line 2 in a collecting tank SO and then through a three-way valve V3 and a line 5 to be recycled through a line 8 to valve V1 in order that the above mentioned mixing and dissolving step is repeated to further lower the polychlorobiphenyl content therein or else it is caused to flow through a line 6 and a circulating pump PC2 in a second set of heaters R2 which are thermostatically controlled at a temperature of 80°C and then in a centrifugal separator SE which is under a vacuum generated by the vacuum pump PV and in which the stripping of the dissolved pyrrolidone rests is performed under an inert gas stream, preferably a nitrogen stream. The PCB containing pyrrolidone is entrained by the nitrogen stream up to the upper outlet of the separator SE, and conveyed to a water cooled condenser RF from where it is discharged

into the drain tank S1 und r the vacuum generated by the vacuum pump PV. The pyrrolidone flowing out of the centrifuge and stored in the tanks SP1 and SP2 in the meantime is recycled to the mixer M through the three-way valve V6, the line 9 and the circulating pump PC4 for its reuse in the dissolving step of the PCB contained in the oil. This recycling step is carried out until the PCB in the pyrrolidone has reached such a percent as to permit a convenient separation by distillation which is carried out in a conventional distillation plant not shown. The oil is drained from the centrifugal separator SE through a line 7 and pumped by means of a circulating pump PC3 through a three-way valve V4 to the drain SC or else recycled through a line 8 to the valve V1 to be again subjected to the so far described treatment.

From the foregoing it will be readily apparent that the method according to the invention permit a decontamination from PCB with very high yields, at any rate within the limits permitted by the harmfulness of the substance.

It should be understood that the invention is not limited to the d-escribed embodiment, but that all the modifications and changes within the scope of the invention can be made thereto.

0109366

CLAIMS

1. Method of decontaminating mineral oils and dielectric silicone fluids from polychlorobiphenyl, characterized in that it comprised the steps of:
- mixing the fluid to be contaminated with a suitable solvent at a suitable temperature in order to dissolve the polychlorobiphenyl and the possible oxidized compounds;
- separating by decantation and/or centrifugation the solvent excess from the fluid under treatment,
- stripping the dissolved rests of solvent from the fluid,
- recovering the solvent by distillation and separating polychlorobiphenyl therefrom.

2. Method as claimed in claim 1, characterized in that said dissolving step of polychlorobiphenyl and possible oxidized compounds contained in the fluid to be decontaminated occurs at a temperature ranging from 50° to 80° C.

3. Method as claimed in claim 1, characterized in that said stripping step is performed under vacuum and in an atmosphere of inert gas, such as nitrogen.

4. Method as claimed in claim 1, characterized in that the mixing and dissolving, decantation and/or centrifugation and/or stripping steps are cyclically carried out until the fluid is fully decontaminated.

5. Method as claimed in claim 1, charact rized in that said solvent is in a liquid condition at the operative temperature, in order to facilitate its mixing with the fluid to be decontaminated, said solvent further presenting a good heat-stability, a good water miscibility, a very small toxicity and a low cost.

6. Method as claimed in claim 1, characterized in that said solvent has a lower boiling temperature both than that of the fluid to be decontaminated and that of polychlorobiphenyl, in order that it can be readily recovered for reuse, said temperature being however higher than the working temperature.

7. Method as claimed in claim 1, characterized in that said solvent has a higher density than that of the fluid to be decontaminated in order to facilitate the decantation and/or centrifugation steps.

8. Method as claimed in anyone of the preceding claims, characterized in that a pyrrolidone or an alkylderivative thereof is employed as a solvent, such as 1-methyl-2-pyrrolidone or 2-pyrrolidone.

European Patent Office

EUROPEAN SEARCH REPORT

0109366
Application number

EP 83 83 0204

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
L	CHEMICAL ABSTRACTS, vol. 99, no. 22, 28th November 1983, page 319, no. 181006u, Columbus, Ohio, US M.A. MAKAREWICZ: "Solvent extraction of polychlorinated biphenyl" & PROC. UCC-ND/GAT ENVIRON. PROT. SEMIN. 1982 (Pub. 1983), (CONF-820418), 301-6 (Cat. O,X)	1	C 10 M 11/00 A 68 D 3/00
A	FR-A- 88 678 (C.F.R.) * Abstract, points 1-3 *	1,8	
A	US-A-2 484 469 (B.B. SCHAEFFER) * Claim 1 *	1	
A	GB-A-2 071 137 (TEXACO) * Claim 1 *	1,8	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
A	US-A-4 299 704 (S.D. FOSS) * Claims 1-13 *	2	C 10 M C 10 G A 62 D C 07 C C 08 G
P,X	US-A-4 387 018 (G.T. COOK) * Claims 1-6 *	1	
P,X	US-A-4 405 448 (J.M. GOOGIN) * Claims 1-8 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-01-1984	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503. 03.82